



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>C09D 7/12, 5/00, C08K 3/22, C09K 3/14</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/52105</b> <b>(43) International Publication Date:</b> 8 September 2000 (08.09.00)
<b>(21) International Application Number:</b> PCT/US00/05671 <b>(22) International Filing Date:</b> 3 March 2000 (03.03.00)  <b>(30) Priority Data:</b> 60/122,661                      3 March 1999 (03.03.99)                      US 60/122,850                      4 March 1999 (04.03.99)                      US  <b>(71) Applicant:</b> SCARLETTE, Terry, Lane [US/US]; 228 East Meadow Road, Thomasville, NC 27360 (US).  <b>(74) Agent:</b> LAMMERT, Steven, R.; Barnes & Thornburg, 11 South Meridian Street, Indianapolis, IN 46204 (US).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.          Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> ABRASION RESISTANT COATINGS  <b>(57) Abstract</b>  <p>A coating composition for forming abrasion-resistant coatings is described. It has been found that sol gel process aluminum oxide grain can be added to a film-forming resin composition for producing coatings exhibiting exceptional abrasion resistance.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

## ABRASION RESISTANT COATINGS

### Field of the Invention

This invention relates to a composition and method for forming  
5 abrasion resistant coatings. More particularly, this invention is directed to novel  
coating compositions containing a sol gel aluminum oxide grain in amounts sufficient  
to provide coatings exhibiting enhanced abrasion resistance.

### Background and Summary of the Invention

10 The application of protective or decorative coatings is a common  
processing step in many manufacturing protocols. One important functional property  
of such coatings, whether they be applied for a decorative or a protective function, is  
abrasion resistance. Disruption of the integrity of the applied coatings by abrasive  
contact with other surfaces during shipment or in the ordinary use of the coated  
15 surfaces can affect the appearance of the coatings and their effectiveness in protecting  
the underlying surface. Accordingly, there has been a significant research and  
development effort directed to the formulation of coating compositions which exhibit  
abrasion resistance along with other desirable coating characteristics such as flexibility,  
hardness, adhesion, transparency, translucency, and the like.

20 Abrasion resistance is a particularly important and desirable property  
for coating formulations used on surfaces which in use are subjected to abrasive  
contacts with other objects, such as flooring, shelving and the like. The use of  
coatings exhibiting good abrasion resistance on such surfaces prolongs both the  
appearance and the functionality of the coating compositions.

25 Therefore, in accordance with this invention there is provided a coating  
composition for forming abrasion resistant coatings. The invention is based, at least in  
part, on the discovery that the use of a sol gel process grain or grain composition as an  
additive at effective levels in a resin coating composition provide coatings exhibiting  
surprisingly enhanced abrasion resistance.

30 Typical coating compositions in accordance with this invention  
comprise a film-forming resin composition and a sol gel process ceramic grain  
composition wherein the ceramic grain contains aluminum oxide and wherein the

-2-

aluminum oxide grain forms about 1 to about 60 percent by weight of the coating. The film-forming resin component of the present coating composition is preferably a thermosetting or UV-curable resin of the type used in decorative and protective coating compositions.

5 In another embodiment of the present invention improved abrasion resistant surface finishes are applied in a coating protocol utilizing at least one sealer or primer coating composition to form a sealer coat and at least one top coat composition to form a surface top coat. The improved surface finish and method comprises using an improved sealer and/or top coating composition comprising a film-forming resin  
10 composition and a sol gel processed ceramic grain in an amount effective to impart abrasion resistance to the surface finish.

#### Detailed Description of the Invention

In accordance with one embodiment of this invention there is provided  
15 a curable coating composition for forming abrasion-resistant coatings. The coating composition comprises a film-forming resin composition, most typically a thermosetting resin or a UV-curable resin, and a sol gel processed grain composition. The film-forming resin composition is formulated to include an amount of a sol gel ceramic grain composition sufficient to enhance the abrasion resistance in the resulting  
20 cured coatings.

In one embodiment of the invention the film-forming resin of the present coating composition is a thermosetting resin composition comprising epoxy resins, acrylic resins, polyester resins, urea resins, melamine resins or polyurethane resins.

25 In another embodiment of the invention the film-forming resin composition comprises a UV-curable resin, typically a UV-curable resin comprising olefin-functional monomers and olefin-functional oligomers and polymers. Typically such formulations include a combination of mono- and multi-functional olefin oligomers or polymers. See, for example, the disclosures of U.S. Patent Nos.  
30 4,600,649; 4,902,975; 4,900,763; and 4,065,587, the disclosures of which are incorporated herein by reference. In one preferred embodiment of the invention there is provided a coating for forming abrasion resistant coating compositions, particularly

for wood floor applications, wherein the coating composition comprises mono-olefin functional and multi-olefin functional polyurethane monomers, oligomers and polymers.

Typically the present coating compositions comprise about 40 to about 5 90 percent by weight of a film-forming resin composition and about 10 to about 60 weight percent of a sol gel process ceramic grain, typically an aluminum oxide composition. Of course, such coating compositions can, and typically do, include other standard coating additives such as resin-dependent curing agents or catalysts, flow aids, wetting agents, dispersing agents, pigments, dyes, fillers, fibers, antistatic 10 agents, lubricants, surfactants, plasticizers, rheology modifiers, and coupling agents. Thus, for example, coating compositions of this invention utilizing UV-curable resins typically include effective amounts (about 0.1 to about 3 percent by weight) of one or more photoinitiators. Such compositions can be cured by electron beam irradiation without photoinitiators.

15 The coating composition may also, for example, contain a coupling agent. Exemplary of such coupling agents suitable for use in this invention include organo silanes, zircoaluminates and titanates. The coupling agent may be added directly to the coating composition. Alternatively, the ceramic grain may be pre-treated with the coupling agent before the grain is added to the coating composition. 20 The coupling agent is added in an amount typically between 0.1 to 5 % by weight of the ceramic particle weight.

The mineral component of the present coating compositions comprises a form of alumina made by sol gel processing. These products, sometimes referred to as sol gel process ceramic grain are commercially available from several sources. In 25 one embodiment of the invention the sol gel processed alumina grain is a product sold under the name Cubitron® by 3M Corporation.

Sol gel processed grain compositions such as those for use in accordance with this invention are often specified, *inter alia*, by grain size, ranging from about JIS 240 down to JIS 8000. These grain sizes correspond to a particle size 30 range from about 130  $\mu\text{m}$  down to about 0.5  $\mu\text{m}$ . The sol process grain component of the present composition can be of a homogeneous grain size or several grain sizes in combination. In one embodiment of the present invention, the sol gel process grain

forms about 1 to about 60 percent by weight of the coating, more typically about 10 to about 40 percent by weight of the coating with a grain size of JIS 320 or smaller. In one embodiment, JIS 400 sol gel process aluminum oxide grain is used alone or in combination with smaller and/or larger grain size material. Sealer coats/primer coats in accordance with the present invention typically have higher weight percents of the grain composition than grain-filled top coat compositions. Top coat compositions are usually formulated to contain about 1 to about 15 percent of the sol gel processed grain while sealer/primer coat composition are most typically formulated to contain about 10 to about 40, more preferably about 10 to about 30 percent by weight of the sol gel process grain.

The ceramic grain particles may also contain a surface coating. Surface coatings are known to improve the adhesion between the ceramic particle and the film-forming resin composition binder in abrasive articles. Such surface coatings are described in U.S. Patent Nos. 5,011,508; 1,910,444; 3,041,156; 5,009,675; 4,997,461; and 5,213, 951.

The coating compositions of the present invention are applied using art-recognized coating application techniques including spray coating, curtain coating, reverse roll coating, vacuum coating, extrusion coating, or direct or differential roll coating applications. The viscosity of the coating compositions of the present invention is not critical; thus, the present invention encompasses coating compositions of any given viscosity containing a film-forming resin composition and a sol gel processed ceramic grain. Typically, the viscosity of the coating compositions can range from about 200 centipoise up to about 8000 centipoise depending on the grain loading the nature of the film-forming resin components of the composition. The compositions are prepared utilizing standard coating formulation techniques. Thus, the ceramic grain composition can be blended into or sifted onto, for example, floor finishing compositions compositions for providing coatings with enhanced abrasion resistance without compromise of other functionally significant properties such as flexibility, hardness, adhesion and the like.

Most surface finishing protocols comprise the steps of applying at least one sealer/primer coating composition to form a sealer/primer coat and one top coating composition to form a surface top coat. The finished surfaces can be prepared

to have improved abrasion resistance using an improved sealer coating or top coating composition in accordance with this invention, *i.e.*, one comprising a film-forming resin composition and a sol gel process ceramic grain in an amount effective to impart enhanced abrasion resistance to the sealer coat. In some coating protocols, for  
5 example, those used in applying coatings for wood flooring, the wood surface is coated with at least two sealer coats, more typically two to five sealer coats prior to application of one or more top coat compositions. The surface finish can be formed to have exceptional abrasion resistance wherein, during the coating process, at least one of the applied sealer coats is a sol process grain filled coating composition of the  
10 present invention. In one embodiment, at least two sealer coats of the present invention are applied to the surface before application of the top coat.

In still another embodiment of this invention, the top coat is a sol gel process grain filled coating composition in accordance with this invention. Top coat formulations typically are formulated to contain lower levels of grain, generally in the  
15 range of about 1 to about 15 percent by weight of fine grain, typically JIS 400 or finer. In one embodiment, the surface being coated is a wood surface intended for use in flooring applications and the film-forming resin composition of both the sealer and top coats are UV-curable 100 percent solids compositions comprising a combination of mono-olefin functional and multi-olefin functional monomers, oligomers and polymers.

20

**Preparation:** Sol gel processed ceramic grain for use in this invention may be made according to the following procedure:

Mixing step: An alumina-based mixture is prepared that comprises an alumina precursor, optionally an acid, and liquid medium. The alumina precursor is  
25 capable of being sintered into alpha alumina. The preferred alumina precursor is alpha alumina monohydrate, commonly referred to as boehmite. Examples of other alumina precursors include alpha alumina powders, gamma alumina powders, aluminum formoacetate, aluminum nitroformoacetate and aluminum salts.

One useful alpha alumina monohydrate is commercially available from  
30 the Alcoa Company. Other alpha alumina monohydrates are commercially available from Condea GmbH, Hamburg, Germany. Preferred alumina monohydrates are in the alpha form, and include relatively little, if any, hydrated phases other than

monohydrates (although very small amounts of trihydrate impurities can be present in some commercial grade boehmite, which can be tolerated). These monohydrates typically have a low solubility in water and have a high surface area (typically at least about 180 m<sup>2</sup>/g).

5                   The liquid medium in which the boehmite mixed is typically water. The water may be tap water, distilled water or deionized water. In some instances, it is preferable to heat the aqueous medium (e.g., 30-70°C) to improve the mixing of the boehmite.

10                   The mixture may further comprise peptizing agents; these peptizing agents are generally soluble ionic compounds which are believed to cause the surface of a particle or colloid to be uniformly charged in the liquid medium (e.g., water). Preferred peptizing agents are acids or acid compounds. Examples of typical acids include monoprotic acids such as acetic, hydrochloric, formic, and nitric acid, with nitric acid being preferred. Typically, the mixture contains at least 0.1 to 20 % by weight, preferably 1 % to 10 % by weight acid and most preferably 3 to 8 % by weight acid, based on the weight of boehmite in the mixture. In some instances, the acid may be applied to the surface of the alpha alumina monohydrate particles prior to being combined with the water.

20                   The mixture may further comprise a nucleating material or nucleating material precursor such as alpha alumina, alpha iron oxide, an alpha iron oxide precursor and/or chromia. Additional details regarding nucleating materials are disclosed, for example, in U.S. Patent Nos. 4,623,364; 4,744,802; 4,964,883; 5,139,978; and 5,219,806. An example of a nucleating material is iron oxide or an iron oxide precursor. Sources of iron oxide, which in some cases may act as or provide a material that acts as a nucleating material, include hematite (i.e.,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), as well as precursors thereof (i.e., goethite ( $\alpha$ -FeOOH), lepidocrocite ( $\gamma$ -FeOOH), magnetite (Fe<sub>3</sub>O<sub>4</sub>), and maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>)).

30                   The alumina mixture may further comprise other metal oxide precursors, sometimes referred to as a metal oxide modifier. The term precursor means that the material is capable of being converting into metal oxide under appropriate sintering conditions. The amount of the metal oxide precursor added to the mixture is calculated and determined based upon the desired amount in the final



sintered mineral particle. These other metal oxides may alter the physical and chemical properties of the resulting mineral particle. The metal oxide precursor may be added to the mixture as 1) a metal salt, 2) a metal oxide particle or 3) a colloidal suspension of the metal oxide. Preferably these precursors are added as a metal salt and examples of metal salts include metal nitrate salts, metal acetate salts, metal citrate salts, metal formate salts, and metal chloride salts. For metal oxide particles, it is generally preferred that the particles are less than 5 microns, preferably less than 1 micron, in size. Colloidal metal oxides are discrete finely divided particles of metal oxide having one or more of their dimensions within a range of about 3 nanometers to about one micrometer. Examples of these colloidal metal oxides include lithium oxide, manganese oxide, zirconium oxide, silica, chromium oxide, praseodymium oxide, dysprosium oxide, samarium oxide, cobalt oxide, zinc oxide, neodymium oxide, yttrium oxide, ytterbium oxide, magnesium oxide, nickel oxide, silica, manganese oxide, lanthanum oxide, gadolinium oxide, dysprosium oxide, europium oxide, ferric oxide, hafnium oxide, and erbium oxide.

Typically, the use of a metal oxide modifier can decrease the porosity of the sintered mineral particle and thereby increase the density. Additionally certain metal oxide precursors may reduce the temperature at which transitional aluminas transform into alpha alumina. Certain metal oxides may react with the alumina to form a reaction product which may be beneficial in enhancing the physical properties of the mineral particle. Thus, the selection and amount of metal oxide will depend, in part, upon the processing conditions and the desired properties of the mineral particle.

Oxides of cobalt, nickel, zinc, and magnesium typically react with alumina to form a spinel, whereas zirconia and hafnia do not react with the alumina. Alternatively, the reaction products of dysprosium oxide and gadolinium oxide with alumina oxide are generally garnet. The reaction products of alumina with praseodymium oxide, ytterbium oxide, erbium oxide, and samarium oxide generally have a perovskite and/or garnet structure. Ytria can also react with alumina to form  $Y_3Al_5O_{12}$  having a garnet crystal structure. Certain rare earth oxides and divalent metal cations react with alumina to form a rare earth aluminate represented by the formula  $LnMA1_{11}O_{19}$ , wherein Ln is a trivalent metal ion such as  $La^{3+}$ ,  $Nd^{3+}$ ,  $Ce^{3+}$ ,  $Pr^{3+}$ ,  $Sm^{3+}$ ,  $Gd^{3+}$ ,  $Er^{3+}$ , or  $Eu^{3+}$ , and M is a divalent metal cation such as  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$ ,

$\text{Zn}^{2+}$ , or  $\text{CO}^{2+}$ . Such aluminates have a hexagonal crystal structure; these aluminates are sometimes referred to as a magnetoplumbite platelets. For additional details regarding the inclusion of metal oxide (and/or precursors thereof) in a boehmite mixture see, for example, in U.S. Patent Nos. 4,314,827; 4,770,671; 4,881,951; 5 5,429,647; and 5,551,963.

The alumina-based mixtures typically comprise greater than 15 % by weight (generally from greater than 30 % to about 80 % by weight) solids, based on the total weight of the mixture. Certain mixtures, however, comprise 35 % by weight or more, 45 % by weight or more, 50 % by weight or more, 55 % by weight or more, 10 60 % by weight or more, as well as 65 % by weight or more solids, based on the total weight of the mixture.

The mixture may be prepared, for example, by gradually adding a liquid medium to a component(s) that is non-soluble in the liquid medium, while the latter is mixing or tumbling. For example, a liquid medium containing water, nitric acid, and 15 metal salt may be gradually added to boehmite, while the latter is being tumbled such that the liquid medium is more easily distributed throughout the boehmite. Alternatively, the mixture may be formed by combining boehmite, water and acid and then mixed to form essentially a homogeneous mixture. Next, nucleating agents and/or metal oxide precursors may be added to this mixture.

20 Suitable mixers include pail mixers, sigma blade mixers, ball mill and high shear mixers. Other suitable mixers are available from Eirich Machines, Inc., Gurnee, IL; Hosokawa-Bepex Corp., Minneapolis, MN (including a mixer available under the trade designation "SCHUGI FLEX-O-MIX", Model FX-160); and Littleford-Day, Inc., Florence, KY.

25 After the alumina-based mixture is formed, the mixture may be heated to increase the dispersibility of the alpha alumina monohydrate and/or to create a homogeneous mixture. The temperature may vary, for example, the temperature may range from about 20 to 80°C, usually between 25 to 75°C. Alternatively, the mixture may be heated under a pressure ranging from 1.5 to 130 atmospheric pressure.

30 The mixture may gel prior to or during the drying step. The addition of most modifiers may result in the mixture gelling faster. The pH of the mixture and concentration of ions in the gel generally determines how fast the mixture gels.

Typically, the pH of the mixture is within a range of about 1.5 to about 4. The gelled mixture may be extruded.

Drying Step: In general, techniques for drying the mixture are known in the art, including heating to promote evaporation of the liquid medium or simply  
5 drying in air. The drying step generally removes a significant portion of the liquid medium from the mixture; however, there still may be a minor portion (e.g., about 10 % or less by weight) of the liquid medium present in the dried mixture. Typical drying conditions include temperatures ranging from about room temperature to over about 200°C, typically between 50 to 150°C. The times may range from about 30 minutes  
10 to several days.

Converting Step: After drying, the dried mixture may be converted into precursor particles. One typical means to generate these precursor particles is by a crushing technique. Various crushing or comminuting techniques may be employed such as a roll crusher, jaw crusher, hammer mill, ball mill and the like. Coarser  
15 particles may be recrushed to generate finer particles.

Alternatively, the dried mixture is shaped into lumps with a high volatilizable content which then are explosively comminuted by feeding the lumps directly into a furnace held at a temperature above 350°C, usually a temperature between 600 to 900°C.

Calcining Step: In general, techniques for calcining the dried mixture or ceramic precursor particles, wherein essentially all the volatiles are removed and the various components that were present in the mixture are transformed into oxides, are known in the art. Such techniques include using a rotary or static furnace to heat dried mixtures at temperatures ranging from about 400 to 1000°C (typically from about 450  
20 to 800°C) until the free water, and typically until at least about 90% by weight of any bound volatiles, is removed.

Impregnating Step: A metal oxide modifier precursor can be impregnated into a calcined precursor particle, although this impregnation step is not required. The metal oxide modifier precursor is selected to provide the desired  
30 characteristic of the mineral particle. Typically, the metal oxide precursor is in the form of metal salts. Metal oxide precursors and metal salts are described above.

Methods of impregnating sol gel-derived mineral particles are described in general, for example, in U.S. Patent No. 5,164,348. In general, ceramic precursor materials (i.e., dried alumina-based mixtures, dried ceramic precursor material, calcined alumina based mixtures or calcined ceramic precursor material) are porous.

5 For example, a calcined ceramic precursor material typically has pores about 5 to 10 micrometers in diameter extending into the material from an outer surface. The presence of such pores allows an impregnation composition comprising a mixture of liquid medium (typically water) and appropriate metal precursor to enter into ceramic precursor material. The impregnation process is thought to occur through capillary

10 action.

The liquid medium used for the impregnating composition is preferably water (including deionized water), an organic solvent (preferably a non-polar solvent), or mixtures thereof. If impregnation of a metal salt is desired, the concentration of the metal salt in the liquid medium is typically in the range from about 5 % to about 40 %

15 dissolved solids, on a theoretical metal oxide basis. Preferably, there is at least 50 ml of solution added to achieve impregnation of 100 grams of porous ceramic precursor material.

After the impregnation step, the resulting impregnated precursor particle is typically calcined a second time to remove any volatiles prior to sintering.

20 Typical calcining conditions are described above.

Sintering Step: After the precursor particle is formed or optionally calcined, the precursor particle is sintered to provide a dense ceramic alpha alumina-based mineral particle. In general, techniques for sintering calcined material, which include heating at a temperature effective to transform transitional alumina(s) into

25 alpha alumina, cause all of the metal oxide precursors to either react with the alumina or form metal oxide, and increase the density of the ceramic material, are known in the art. The calcined material may be sintered by heating (e.g., using electrical resistance, microwave, plasma, laser, or gas combustion both in batch or continuous processes). Sintering temperatures usually range from about 1200 to 1650°C, typically, from

30 about 1200 to 1500°C. The length of time which the calcined material is exposed to the sintering temperature depends, for example, on particle size, composition of the particles, and sintering temperature. Typically, sintering times range from a few

-11-

seconds to about 60 minutes (preferably, within about 3 to 30 minutes). Sintering is typically accomplished in an oxidizing atmosphere, although neutral or reducing atmospheres may also be used.

Crushing and Classification Steps: In some instances, the mineral  
5 particle is sintered to about the desired particle size and about the desired particle size distribution. The mineral particle may be further classified using screening techniques, air classification techniques or water classification techniques to further refine the particle size distribution. In some cases, the mineral particle is first crushed to a  
10 smaller particle size. This crushing may be accomplished for example, by roll crushing, jet milling, hammer milling, ball milling and the like. After crushing, the resulting particles are typically classified using screening techniques, air classification techniques or water classification techniques to further refine the particle size distribution.

The aluminum sol gel ceramic grain can also be made by other procedures known in the art and described in each of the following U.S. Patents which  
15 are specifically incorporated herein by reference: U.S. Patent Nos. 4,623,364; 4,314,827; 4,744,802; and 4,800,685.

#### Sintered Alumina Mineral Particle Properties

The sintered alumina mineral particles have a true density of at least  
20 about 3.70 grams/cm<sup>3</sup>, preferably at least about 3.80 grams/cm<sup>3</sup>, more preferably at least about 3.85 grams/cm<sup>3</sup>, and most preferably at least about 3.90 grams/cm<sup>3</sup>. Likewise, it is preferred that the sintered alumina mineral particles have a theoretical density of at least about 90 %, preferably at least about 93 % and more preferably at least about 95 %. The densities of the particles may be determined with a helium gas  
25 pycnometer (available under the trade designation "Micromeritics AccuPyc 1330" from Micromeritics Instruments Corp., Norcross, Ga.).

The sintered alumina mineral particles have a hardness of at least about 16 GPa, preferably at least about 17 GPa, more preferably at least about 18 GPa and most preferably at least about 19 GPa. In some instances, the hardness may be greater  
30 than about 20 GPa or greater than about 22 GPa. The hardness may be measured according to a Vicker's indentation method using a 500 gram weighted stylus. This

test procedure is further described in accordance with ASTM (American Society of Testing Methods) Test Method E3 84.

The sintered alumina mineral particles have a toughness of at least about  $2\text{MPa}\cdot\text{m}^{0.5}$ , preferably at least about  $2.2\text{MPa}\cdot\text{m}^{0.5}$ , more preferably at least about  $2.5\text{MPa}\cdot\text{m}^{0.5}$ , and most preferably at least about  $2.8\text{MPa}\cdot\text{m}^{0.5}$ . In some instances, the toughness may be greater than about  $3.0\text{MPa}\cdot\text{m}^{0.5}$ , or greater than about  $4.0\text{MPa}\cdot\text{m}^{0.5}$ . The toughness may be measured according to a Vicker's indentation method using a 500 gram weighted stylus. The toughness may be measured according to a test procedure outlined in "Equilibrium Penny-Like Cracks in Indentation Fracture" by BR Lawn and ER Fuller published in the Journal of Material Science, Volume 10, 1974, pages 2016-2024.

#### EXAMPLE 1

##### ABRASION RESISTANT COATING COMPOSITION

The following coating composition is exemplary of a UV-curable coating composition used, for example, in floor finishing. The first step in preparation was to blend the following components:

Ingredient % by Weight	Ingredient Name	Ingredient Type
6.14	1,6 hexanediol diacrylate	Difunctional acrylate oligomer
6.46	Photomer 4149 SR454	Trifunctional acrylate oligomer
6.30	V-Pyrol, Caustic	Monofunctional monomer
3.89	Sartomer CN 292	Tetrafunctional polyester acrylate
3.55	Photomer 3016-20R	Epoxy acrylate
1.70	Darocur 1173	Photoinitiator
7.27	BYK-361	Acrylated silicon flow agent
35.30	Sartomer CN 971A80	Acrylated aromatic urethane
1.05	Benzophenone-flakes	Photoinitiator

The above ingredients were then mixed for 20 minutes and thereafter the following components were sifted into the mix with blending:

-13-

Ingredient % by Weight	Ingredient Name	Ingredient Type
0.24	R-972 Aerosil	Precipitated silica (rheology modifier)
28.11	Cubitron MFM-321 (3M Corporation)	Sol gel process ceramic aluminum oxide mineral

5

The resulting mixture was blended for 20 minutes at high speed to achieve a smooth consistency.

10 The above-described UV-curable coating composition of this invention was applied to wood surfaces and UV-cured to provide coatings exhibiting enhanced abrasion resistance in comparative abrasion resistance testing. The coating composition can be applied to a surface by any art-recognized methods including, but not limited to, the use of a brush, the use of a spray device, the use of a roller, and the like.

## EXAMPLE 2

## ABRASION RESISTANT COATING COMPOSITION

A similar procedure to that described in Example 1 was used to prepare a UV-curable coating composition except that the following ingredients were blended:

5

10

15

Ingredient % by Weight	Ingredient Name	Ingredient Type
11.08	Tripropylene glycol diacrylate	Difunctional acrylate oligomer
17.87	1,6 hexanediol diacrylate	Difunctional acrylate oligomer
14.86	Trimethylolpropane trimethacrylate	Trifunctional acrylate oligomer
20.29	Sartomer CN-975	Tetrafunctional aromatic urethane acrylate
2.40	Darocur 1173	Photoinitiator
1.35	BYK-P105	Anti-settling agent
0.12	Sartomer CN 971A80	Acrylated aromatic urethane
30.61	Benzophenone-flakes	Photoinitiator

The above ingredients were then mixed for 20 minutes and thereafter the following components were sifted into the mix with blending:

20

Ingredient % by Weight	Ingredient Name	Ingredient Type
1.42	Cubitron MFM-321 (3M Corporation)	Sol gel process ceramic aluminum oxide mineral

The resulting mixture was blended for 20 minutes at high speed to achieve a smooth consistency and applied to wood surfaces as described in Example 1.

25



-15-

## EXAMPLE 3

## ABRASION RESISTANT COATING COMPOSITION

A similar procedure to that described in Example 1 was used to prepare  
5 a UV-curable coating composition except that the following ingredients were blended:

	Ingredient % by Weight	Ingredient Name	Ingredient Type
10	10.00	Isobonyl acrylate	Monofunctional monomer
	8.00	Tripropylene glycol diacrylate	Monofunctional monomer
	8.00	Trimethylpropane trimethylacrylate	Monofunctional monomer
	17.50	aromatic urethane	oligomer
	17.50	aliphatic urethane	oligomer
15	2.00	Trimethylbenzophenone	photoinitiator
	2.00	Alpha hydroxy ketone	photoinitiator
	2.00	BYK-331	flow aid
	1.00	BYK-A500	defoaming agent
	2.00	Disperbyk	wetting agent

20 The above ingredients were then mixed for 20 minutes and thereafter the following components were sifted into the mix with blending:

	Ingredient % by Weight	Ingredient Name	Ingredient Type
25	30.00	Cubitron MFM-321 (3M Corporation)	Sol gel process ceramic aluminum oxide mineral

The resulting mixture was blended for 20 minutes at high speed to achieve a smooth consistency and applied to wood surfaces as described in Example 1.

30

## EXAMPLE 4

## WEAR RESISTANCE TESTS OF ABRASIVE COATING COMPOSITIONS

The abrasion resistant coating composition described in Example 1 was subjected to the various wear resistance tests described below. The test results were as follows:

Taber Wear Resistance Test

A Taber Wear Resistance Test was performed on the coating composition described in Example 1. The coating composition was applied to either a sliced engineered product or a sliced face engineered product (designated sliced 1 and sliced 2, respectively) or to a rotary engineered product or a rotary faced engineered product (designated rotary 1 and rotary 2, respectively) and initial and final wear were tested using a standard Taber Wear Resistance Test. This test determines abrasion resistance of coatings to abrasion produced by a Taber Abrasion Machine. Briefly, the test required measuring the initial coating thickness of the test specimen in several places. The test specimen was then mounted on a turntable and the abrading heads of the Taber Abrasion Machine were placed on the test specimen and the test specimen was subjected to abrasion until wear-through occurred. The abrading heads of the Taber Abrasion Machine were CS-0 wheels fitted with S-33 sandpaper strips and each wheel was weighted with a 500 gram weight. "Initial Wear" indicates the number of cycles to observe wear-through in any test area of the test specimen while "Final Wear" indicates the number of cycles required to observe wear-through in all test areas of the test specimen. Wear conversion was calculated by dividing the number of cycles to wear-through by the film thickness and is expressed below as the number of cycles required to remove a millimeter of coating thickness. Thus, wear conversion is an indication of abrasion resistance and the higher the wear conversion value the greater the abrasion resistance.

-17-

Sample	Initial Wear	Final Wear	Film Thickness	Wear Conversion
Sliced 1	550 cycles	855 cycles	1.74 mils	491.38 cycles/mil
Sliced 2	1040 cycles	1075 cycles	1.64 mils	655.49 cycles/mil
Rotary 1	1035 cycles	1080 cycles	1.66 mils	650.6 cycles/mil
Rotary 2	1525 cycles	1646 cycles	1.75 mils	940.57 cycles/mil

#### Crosshatch Adhesion Test

The crosshatch adhesion values were determined using a Gardco Crosshatch Cutter and standard tape. This test involved scratching a crosshatched pattern of squares onto the surface of a product to which the coating composition described in Example 1 was applied. Tape was then applied over the pattern of squares and was subsequently removed to determine the number of squares removed by the tape. The test provides an indication of the capacity of the coating composition to adhere to surfaces.

Sample	% Adhesion	Adhesion Rating
Sliced 1	94.8	38
Sliced 2	93.4	38
Rotary 1	99.6	48
Rotary 2	99.2	48

#### Scrape Adhesion Test

The scrape adhesion was determined using a Balanced Beam Adhesion Tester fitted with a barrel scrape apparatus. Mass was added until a scrape through the finish was observed.

-18-

Sample	Mass for Scrape (grams)
Sliced 1	900
Sliced 2	950
Rotary 1	1300
Rotary 2	1700

## EXAMPLE 5

## GLOSS AND ACETONE CURE TESTS

The abrasion resistant coating composition described in Example 1 was subjected to gloss and acetone cure tests as described below. The coating composition was first applied to either a sliced engineered product or a sliced face engineered product (designated sliced 1 and sliced 2, respectively) or to a rotary engineered product or a rotary faced engineered product (designated rotary 1 and rotary 2, respectively). The test results were as follows:

Gloss Test

The gloss was determined using a 60 degree glossmeter.

Sample	Gloss
Sliced 1	64.5
Sliced 2	66.9
Rotary 1	66.5
Rotary 2	61.5

Acetone Cure Test

The acetone cure test was performed by soaking gauze with acetone, placing the acetone soaked-gauze on the test samples, and covering the gauze with a glass plate and 10 pounds of weight for 15 minutes to determine if the coatings on the test samples were completely cured.

-19-

Sample	Acetone Pass/Fail
Sliced 1	Pass
Sliced 2	Pass
Rotary 1	Pass
Rotary 2	Pass

## EXAMPLE 6

COMPARISON OF WEAR RESISTANCE OF ABRASION RESISTANT  
COATINGS WITH COMMERCIALY AVAILABLE PRODUCTS

The abrasion resistant coating compositions described in Examples 1 and 3 were subjected to Taber Wear Resistance tests along with three commercially available products for comparison of wear resistance. The Taber Wear Resistance test was performed as described in Example 4 except that the abrasive wheels of the Taber Abrasion Machine were CS-17 wheels (covered with abrasive tape standard to CS-17 wheels), wheels fitted with S-42 sandpaper, or wheels fitted with abrasive S-39 leather as indicated in the table below. The abrasive wheels were weighted with weights of 500 or 1000 grams as also indicated in the table. The coating compositions described in Examples 1 and 3 were designated samples 1 and 2, respectively. The test results were reported as cycles to wear-through and were as follows:

-20-

Sample	CS-17 wheels and 1000 gram weights	S-42 sandpaper and 500 gram weights	S-39 leather and 1000 gram weights
Sample 1	5300 cycles	300 cycles	1600 cycles
Sample 2	3300 cycles	1200 cycles	1000 cycles
Commercial Product 1	3000 cycles	600 cycles	1500 cycles
Commercial Product 2	2000 cycles	1000 cycles	1000 cycles
Commercial Product 3	1800 cycles	75 cycles	1000 cycles

The results shown in the table demonstrate that samples 1 and 2 have enhanced wear resistance in a Taber Wear Resistance test where CS-17 abrasive wheels and 1000 gram weights were used.

CLAIMS:

1. A coating composition for forming abrasion-resistant coatings, said coating composition comprising a film-forming resin composition and a sol gel process ceramic grain composition wherein the ceramic grain contains aluminum oxide, wherein the aluminum oxide grain forms about 1 to about 60 percent by weight of the coating, and wherein the aluminum oxide grain ranges from about 0.5  $\mu\text{m}$  to 130  $\mu\text{m}$  in size.
2. The composition of claim 1 wherein the film-forming resin composition comprises a thermosetting resin.
3. The coating composition of claim 2 wherein the thermosetting resin comprises epoxy resins, acrylic resins, polyester resins, urea, melamines or polyurethane resins.
4. The composition of claim 1 wherein the film-forming resin composition comprises a UV-curable resin.
5. The composition of claim 4 wherein the UV-curable resin comprises olefin functional monomers and olefin functional oligomers or polymers.
6. The coating composition of claim 5 wherein the olefin functional oligomers or polymers comprise polyurethanes.
7. The coating composition of claim 1 wherein the sol gel process ceramic grain composition comprises alumina.
8. The composition of claim 7 wherein the sol gel processed alumina forms about 10 to about 40 weight percent of the coating.
9. In a method of finishing a surface comprising the steps of applying at least one sealer coating composition to form a sealer coat and/or at least one top coating composition to form a surface top coat, the improvement which comprises using an improved sealer and/or top coating composition comprising a film-forming resin composition and a sol gel processed ceramic grain in an amount effective to impart abrasion resistance to the surface finish.
10. The improved method of claim 9 wherein at least two sealer coats are applied to the surface before the top coat is applied.

11. The improved method of claim 9 or 10 wherein the coating composition for the top coat comprises a film-forming resin composition and a sol gel process ceramic grain.
12. The improved method of claim 9 wherein the sealer coat or top  
5 coat is formed using the coating composition wherein the film-forming resin composition comprises a thermosetting resin.
13. The improved method of claim 9 wherein the sealer coat or top coat is formed using a coating composition wherein the film-forming resin composition comprises a UV-curable resin composition.
- 10 14. The improved method of claim 13 wherein the UV-curable resin composition comprises olefin functional monomers and olefin functional oligomers or polymers.
- 15 15. The improved method of claim 14 wherein the olefin functional oligomers or polymers comprise polyurethanes.
16. The improved method of claim 9 or 10 wherein the  
thermosetting resin comprises epoxy resin, a polyurethane resin, a polyester resin or an acrylic resin.
17. The improved method of claim 9 wherein the sol gel process ceramic grain in the sealer coating composition comprises alumina.
- 20 18. The improved method of claim 17 wherein the sol gel processed alumina forms about 1 to about 60 percent by weight of the sealer coat.
19. The improved method of claim 18 wherein the sol gel process alumina forms about 1 to about 15 percent by weight of the top coat.
20. The improved method of claim 9 wherein the surface is a wood  
25 surface.
21. The improved method of claim 9 wherein the surface is metal, plastic, paper, composite fiberboard or vinyl.



# INTERNATIONAL SEARCH REPORT

Intern: al Application No

PCT/US 00/05671

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D7/12 C09D5/00 C08K3/22 C09K3/14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D C08K C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 199722 Derwent Publications Ltd., London, GB; Class A14, AN 1997-241929 XP002141757 & JP 09 078002 A (TOYO INK MFG CO LTD), 25 March 1997 (1997-03-25) abstract	1-3,7,8
A	US 5 780 525 A (SUNG AN-MIN J ET AL) 14 July 1998 (1998-07-14) abstract column 4, line 19 - line 24 column 5, line 50 - line 67 column 6, line 38 - line 62 column 7, line 26 - line 46 --- -/--	1-8

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

4 July 2000

Date of mailing of the international search report

18/07/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo.nl,  
Fax: (+31-70) 340-3016

Authorized officer

Schlicke, B

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 00/05671

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 395 088 A (NORTON CO) 31 October 1990 (1990-10-31) claims 1,2,7 page 3, line 5 - line 12 page 6, line 15 - line 28 ----	1-21
A	WO 97 48774 A (KUMEGAWA MASAHIRO ;OKA NORITOSHI (JP); ARAKI TAKAYUKI (JP); DAIKIN) 24 December 1997 (1997-12-24) & EP 0 909 800 A (DAIKIN INDUSTRIES, LTD) 21 April 1999 (1999-04-21) abstract page 9, line 15 - line 52 ----	1-8
A	EP 0 853 095 A (ALCAN INT LTD) 15 July 1998 (1998-07-15) claims 1,3-5,8 page 2, line 45 - line 46 -----	1-8

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/05671

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 9078002	A	25-03-1997	NONE	
US 5780525	A	14-07-1998	US 5962608 A	05-10-1999
EP 0395088	A	31-10-1990	US 5103598 A	14-04-1992
			AT 154381 T	15-06-1997
			AU 620510 B	20-02-1992
			AU 5390390 A	01-11-1990
			BR 9002016 A	13-08-1991
			CA 2015547 A,C	28-10-1990
			CN 1046925 A,B	14-11-1990
			DE 69030895 D	17-07-1997
			DE 69030895 T	22-01-1998
			DK 395088 T	05-01-1998
			ES 2101680 T	16-07-1997
			GR 3024694 T	31-12-1997
			JP 2528197 B	28-08-1996
			JP 3170270 A	23-07-1991
			KR 139202 B	28-04-1998
			MX 167688 B	05-04-1993
			NO 175970 B	03-10-1994
			US 5185012 A	09-02-1993
			ZA 9003146 A	27-11-1991
WO 9748774	A	24-12-1997	EP 0909800 A	21-04-1999
EP 0853095	A	15-07-1998	EP 0953006 A	03-11-1999
			WO 9830625 A	16-07-1998